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RF Project 766261/719844
Technical Report

STABLE COMPOSITIONS FOR FLUORIDE GLASSES

P. K. Gupta
Department of Ceramic Engineering

For the Period
January 1, 1988 - March 31, 1988

NAVAL RESEARCH LABORATORY
Washington, D.C. 20375

Contract No. N00014-87-C-2186

April 1988

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The Ohio State University
Research Foundation
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Columbus, Ohio 43212

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Introduction

This research contract is part of the NRL effort to produce ultralow-loss long-length fluoride glass fibers. A previous report described the work done in 1987. This interim report describes the progress in the first quarter of 1988.

Objectives of the Project

There are two distinct objectives:

1. Composition Search

   o To explore new fluorozirconate glass compositions more stable than the current composition in use at NRL.

2. Process Modeling

   o To determine the relative influences of various material and process parameters on the crystals in preforms and fibers. (JES)

Results

1. A completely enclosed facility to melt halide glasses in controlled environments (principally Argon and oxygen) has been successfully completed. Reference ZBLAN composition was melted successfully many times to optimize the melting procedure (i.e., the amount of ammonium bifluoride, the flow rate of Argon, and the use of oxygen at the end of melting). The optimized melting schedule is described in Appendix I.

2. Several new compositions have been melted. Table I lists these compositions. Each composition has been melted at least two times.

3. Table II summarizes the optical quality of the bulk glass samples. From these results it appears that the stable glass forming region extends (starting from the reference composition)

   (i) at least 4 mole % towards the ZrF_4 direction,

   (ii) less than 4 mole % towards the BaF_2 direction, and

   (iii) less than 4 mole % towards the LaF_3 direction.

4. Computer modeling of the preform-making process is being carried out following the strategy and procedure which was described in detail in the previous report. Modeling has been completed for Phase I, which consists of solving two coupled non-linear equations for the case of a cylinder (i) heat equation (modified to include the latent heat of crystallization as a heat source term) with convective boundary conditions, and (ii) the equations for nucleation and growth kinetics.

5. The input parameters include material parameters (including those appearing in the theory of classical nucleation and growth -- again see details in the previous report) and several process parameters (radius of preform, heat transfer coefficient, initial temperature of melt). The values of these parameters and the reasons for choosing these values are described in detail in the previous report. However, the values can be readily adjusted when better data become available.

6. The output of the program gives as a function of time of cooling:

   (i) temperature as a function of radial position,

   (ii) volume fraction of crystals as a function of radial position,

   (iii) maximum size of crystal and the number density of crystals as a function of radial position, and

   (iv) the overall volume fraction of crystals in the cylinder.

7. The program has been successfully tested for internal consistencies, for consistencies of the output data, and for the stability of the solution against discretization of the equations (inherent in numerical analysis) and round-off errors.

8. The key modeling results thus far include:

   (i) the temperature may not decrease monotonically with time as a consequence of the heat of crystallization, and

   (ii) volume fraction of crystals is extremely sensitive to the ratio of thermal conductivity of the melt and the product of the heat transfer coefficient and preform radius. Some of these results were discussed with Drs. Aggarwal and Lu recently. Details of these results will be given in the next report.

Plans for April 1988 through June 1988

1. Finish exploration of ZBLAN system (May 15, 1988).

2. Investigate the effect of substitution of K for Na (June 1, 1988).

3. Examination of optical quality (June 15, 1988).

4. Use of simplex optimization technique to determine the best composition (June 15, 1988).

5. Model the crystallization behavior of preform as a function of

   (a) time dependent heat transfer coefficient (May 15, 1988), and

   (b) important material parameters (June 15, 1988).

Table I. ZBLAN Compositions

(Mole %)

		ZrF_4	BaF_2	LaF_3	AlF_3	NaF
*	Z1	57.00	18.29	3.66	2.74	18.30
*	Z2	61.00	16.60	3.32	2.49	16.60
*	Z3	65.00	14.89	2.98	2.23	14.89
*	Z4	69.00	13.19	2.64	1.98	13.19
*	B1	50.35	24.00	3.80	2.85	19.00
*	B2	47.70	28.00	3.60	2.70	18.00
**	B3	45.05	32.00	3.40	2.55	17.00
**	B4	42.40	36.00	3.20	2.40	16.00
*	L1	50.79	19.17	8.00	2.88	19.17
*	L2	48.58	18.33	12.00	2.75	18.33
**	L3	46.38	17.50	16.00	2.62	17.50
**	L4	44.17	16.67	20.00	2.50	16.67
	A1	50.81	19.18	3.84	7.00	19.18
	A2	48.63	18.35	3.67	11.00	18.35
	A3	46.44	17.53	3.51	15.00	17.53
	A4	44.26	16.70	3.34	19.00	16.70
	N1	50.35	19.00	3.80	2.85	24.00
	N2	47.70	18.00	3.60	2.70	28.00
	N3	45.05	17.00	3.40	2.55	32.00
	N4	42.40	16.00	3.20	2.40	36.00
	B-1	55.65	16.00	4.2	3.15	21.00
	B-2	58.30	12.00	4.4	3.3	22.00
	L-1	54.104	20.42	2.0	3.063	20.42
	L-2	55.208	20.842	0.0	3.126	20.842
*	Reference	53	20	4	3	20

* compositions studied
** compositions ruled out from study

Table II. Optical Quality of Bulk Glass Samples

	Sample #	Visual (VC,C,M,B,VB)	Optical Grade	Top Surface Crystal (G,M,B,VB)	Bottom Surface Crystal (VG,G,M,B,VB)	Comments
REF	3-7-88	C-M	A1	B	VB	Many bubbles in bulk-10 per field of view.
REF	3-10-88	C	A1 below .6mm	M	M	Bow ties, hexagons, and ellipses present.
REF	3-16-88	VC	A1	G-M	VG	Best sample.
REF	3-25-88 15g	C	A1	B	M	Bow ties and hexagons present.
Z1	3-30-88	VC	A1 below .6mm	M	VG	Cannot determine X-stal shape.
Z1	3-31-88	C	A1-2	M	M	One side of glass plug is noticeably more crystallized.
Z2	4-1-88	C	A3	B	M	Crystals preferentially oriented radially.
Z2	4-8-88	C	A1	M	M	Ellipse, bow ties, and flower crystals present.
Z3	4-4-88	C-M	A6S	B	M	Few bubbles on bottom, small crystals ruined rating.
Z3	4-11-88	M-B	A4L	B	B	Better than 4-4-88, most crystals are very large.
Z4	4-5 & 6-88	B	A5	VB	B	Bulk crystals large 200u, difficult to rate.
B1	4-7-88	B	A6	M	VB	Top half fairly good glass, bottom half crystallized.
B2	4-12-88	VB	A10	VB	VB	Totally crystallized.
B2	4-13-88	VB	A10	VB	VB	Totally crystallized.
L1	4-14-88	B			B	Bottom half totally crystallized.

VC = Very Clear
C = Clear
M = Medium
B = Bad
VB = Very bad

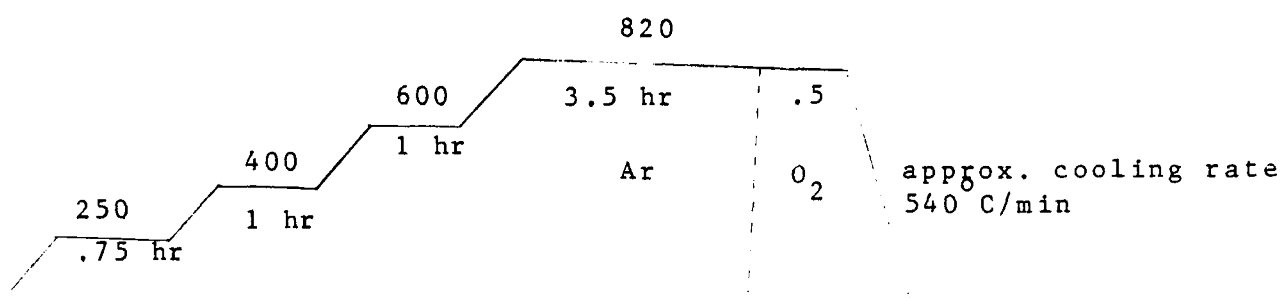
VG = Very Good
G = Good
M = Medium
B = Bad
VB = Very Bad

S = Small Crystals
L = Large Crystals

Appendix I

Melting Procedure

1. Weigh constituents and mix.
2. Weigh and mix NH_4HF_2 to batch in crucible.
3. Place batch in melting apparatus and seal tube.
4. Adjust Ar to .3 l/min for first 45 minutes then reduce to .1 l/min. just to ensure atmosphere.
5. After 6.25 hours change atmosphere to oxygen at .3 l/min.
6. Raise crucible and quench with Ar at 1.3 l/min.



7. Further tests will be conducted to determine exact cooling rate.